DOE AWARD DE-FC26-03NT41974

QUANTUM WELL THERMOELECTRICS FOR CONVERTING WASTE HEAT TO ELECTRICITY

QUARTERLY TECHNICAL PROGRESS REPORT

REPORTING PERIOD 10-1-2006 THROUGH 12-31-2006

Submitted By

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ABSTRACT

New thermoelectric materials using Quantum Well (QW) technology are expected to increase the energy conversion efficiency to more than 25% from the present 5%, which will allow for the low cost conversion of waste heat into electricity.

Hi-Z Technology, Inc. has been developing QW technology over the past six years. It will use Caterpillar, Inc., a leader in the manufacture of large scale industrial equipment, for verification and life testing of the QW films and modules.

Other members of the team are Pacific Northwest National Laboratory, who will sputter large area QW films. The Scope of Work is to develop QW materials from their present proof-of-principle technology status to a pre-production level over a proposed three year period. This work will entail fabricating the QW films through a sputtering process of 50 μm thick multi layered films and depositing them on 12 inch diameter, 5 μm thick Si substrates.

The goal in this project is to produce the technology for fabricating a basic 10-20 watt module that can be used to build up any size generator such as: a 5-10 kW Auxiliary Power Unit (APU), a multi kW Waste Heat Recovery Generator (WHRG) for a class 8 truck or as small as a 10-20 watt unit that would fit on a daily used wood fired stove and allow some of the estimated 2-3 billion people on earth, who have no electricity, to recharge batteries (such as a cell phone) or directly power radios, TVs, computers and other low powered devices.

In this quarter Hi-Z has continued fabrication of the QW films and also continued development of joining techniques for fabricating the N and P legs into a couple. The upper operating temperature limit for these films is unknown and will be determined via the isothermal aging studies that are in progress. We are reporting on these studies in this report. The properties of the QW films that are being evaluated are Seebeck, thermal conductivity and thermal-to-electricity conversion efficiency.

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2 INTRODUCTION

Fabrication development of high efficiency quantum well (QW) thermoelectric continues with the P and N-type Si/SiGe films on Kapton and Si substrate.

Measurement confirmation were perform by Prof. Prab Bandaru of University of California, San Diego (UCSD). The Seebeck coefficient (") and the electrical resistivity (ρ) of $Si/Si_{0.8}Ge_{0.2}$ multilayer films (of approximate thickness 1 μm) deposited by sputtering on Silicon substrates (~ 500 μm) were measured. Liquid metal (InGa) was used to contact the two ends of the sample (as shown below) while the voltage was probed by two needles (from an Alessi 4-probe apparatus) along the length of the sample (as shown below), for 4-point measurement of the in-plane resistivity ($\rho_{||}$).

3 MEASUREMENTS CONFIRMATION BY UCSD

$Si/Si_{0.8}Ge_{0.2}$ Quantum Well (QW) films, 10 nanometers (100 Angstroms) thick were sputter deposited on a 500 μm thick Si substrate (ρ_{Si} ~ 25 Ω cm and a Seebeck coefficient - α_{Si}, ~ 600 μV/K). The purpose of the measurements and evaluation was to determine the " and ρ of the Si/SiGe films. Since the films cannot be measured directly, their values were obtained by measuring the " and ρ of the Si substrate and the " and ρ of the composite. Knowing these two sets of values, the " and ρ values of the films can be readily calculated.

The Seebeck coefficient (") and the electrical resistivity (ρ) of $Si/Si_{0.8}Ge_{0.2}$ multilayer films (of approximate thickness 1 μm) deposited by sputtering on Silicon substrates (~ 500 μm) were measured. Liquid metal (InGa) was used to contact the two ends of the sample (as shown below) while the voltage was probed by two needles (from an Alessi 4-probe apparatus) along the length of the sample (as shown below), for 4-point measurement of the in-plane resistivity ($\rho_{||}$).

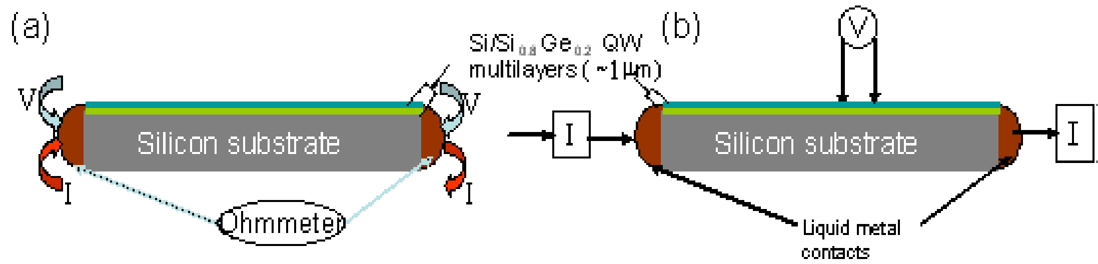

Figure 1 Schematic of the measurement setups for obtaining the resistance (R) of the Si/SiGe multilayers on Si substrates using:
(a) two-terminal Ohmmeter (Tegam Inc.) probes, and
(b) A four probe arrangement, where the current is sent through the liquid metal contacts at the ends while the voltage is measured along the sample with two more probes.
The resistivity parallel to the layers ($\rho_{||}$) is then calculated from measured resistance (R) through the sample geometry, as in the text. The lateral dimensions of the sample are 1.2 cm X 0.6 cm, and the thickness of the Si/SiGe multilayers are ~ 1 μm (The Si substrate is ~ 500 μm thick).

When two probe resistance measurements were performed with an Ohmmeter (from Tegam Inc.) (see Figure 1a), using liquid metal (InGa) contacts at the ends of the sample a resistance of ~ 15 Ω was measured, with a corresponding $\rho_{||}$ = 750 μΩ cm/ 0.75 mΩ cm. Here, we use the formula for $\rho_{||} = R(A/\,l\,)$ with the cross-sectional area (A) = 6C 10^{-5} cm^2 (0.6 cm X 10^{-4} cm) and length (l = 1.2 cm). It is to be noted that the liquid metal contacts *at the ends* were prepared with great care (i.e., prior to placing the liquid metal contacts, the ends were cleaned through argon gas ion milling *in situ* in the chamber, and upon removal from the chamber immediately coated with the liquid metal), to (a) minimize the contact resistance at the InGa/sample interface and (b) permit more of the Si/SiGe QW films to be directly contacted.

When the I and V leads were connected to an LR 700 AC resistance bridge (as in Figure 1b- the current (I) leads are connected to the liquid metal contacts and the voltage probes (V) are contacted only by pressure) a resistance ~ 0.11 Ω was indicated. Assuming again that $\rho_{||} = R(A/\,l\,)$, with the cross-sectional area (A) = 6C 10^{-5} cm^2 (0.6 cm X 10^{-4} cm) and length (l = 0.15875 cm), $\rho_{||}$ = 41.6 μΩ cm. The measured resistance was found to be linear with the distance between the voltage probes, which seems to indicate that current flow is uniform along the sample length.
In this report, we take a mean value of ~ 0.4 mΩ cm from the two measurements. The difference between the 4-probe LR700 and the 2-probe ohmmeter measurement could be due to the effect of the probe and lead contact resistance and should be better characterized. It is to be noted in the above calculations that the contribution of the Si substrate ($R_{substrate}$) to the total measured resistance (Figure 1), R_{total} is neglected due to the much larger resistivity, of the substrate, ~ 25 Ω cm, which is a factor of ~ 6C10^4 larger than the Si/SiGe multilayers resistivity, from:

The low values of $\rho_{||}$ obtained could probably correspond to electronic conduction through

$$\frac{1}{R_{total}} = \frac{1}{R_{substrate}} + \frac{1}{R_{Si/SiGe}}$$

the SiGe layers of the QW superlattice and are remarkably low. If it is assumed that the electronic conduction is taking place entirely through the $Si_{0.8}Ge_{0.2}$ layers, we calculate a carrier concentration of ~ $3\times10^{19}/cm^3$ (μ_n for $Si_{0.8}Ge_{0.2}$ ~ 533 cm^2/Vs[1]) which is similar to conventional bulk SiGe alloys. For the Seebeck measurements, the two ends of the sample were differentially heated by a solder iron, with connected thermocouples and the voltage drop simultaneously measured at the same points. An α (= $\Delta V/\Delta T$) of ~ 1300 μV/K was seen (corresponding to a measured ΔV of ~ 39 mV for a temperature differential (ΔT) of ~ 30 K between the two ends. It was also observed that the Seebeck coefficient has a positive temperature coefficient, increasing with temperature, characteristic of transition to a more insulating material. The power factor for this sample is:

$$\alpha^2/\rho = (1300\ \mu V/K)^2/(0.4\ m\Omega\text{-}cm) = 4225\ \mu W/cm\text{-}K^2$$

For comparison the power factor for Bi_2Te_3 is ~$50\mu W/cm\text{-}K^2$. The Si substrate has high thermal conductivity of ~1.2 W/cm-K, therefore, the total or composite thermal conductivity of this sample (1μm film plus the 500 μm thick Si substrate) would be dominated by the much thicker substrate. So, the room temperature ZT for the composite sample is:

$$ZT = (\alpha^2/\rho)(1/\kappa)T = (4225\ \mu W/cm\text{-}K^2)(1/1.2\ W/cm\text{-}K)(300K) \cong 1.1$$

The composite thermal conductivity could be lowered by using thinner Si substrate or other substrate such as poly crystalline Si or SiGe. Following table show what the room temperature ZT of the1μm plus the substrate be with different substrates:

Substrate	**Substrate Thickness**	**Room Temperature Composite ZT**
Single crystal Si substrate	500μm	**~1**
Single crystal Si substrate	100μm	**~2**
Poly crystal Si substrate	500μm	**~10**
SiGe substrate	500μm	**> 10**

The values of α and $\rho_{||}$ obtained compare much better than previously measured superlattice (SL) materials by others, *viz.,*

(i) Bi_2Te_3/Sb_2Te_3 SL, an α ~ 240 μV/K and $\rho_{||}$ = 948 μΩ cm was reported[2], and

(ii) n-type PbSeTe quantum dot superlattices[3], where it was seen that α ~ 220 μV/K with a resistivity ~ (1.2 - 1.4 mΩ cm).

The large value for the Seebeck coefficient (α) obtained in the present measurements is especially intriguing as it exceeds the values for both the n- $Si_{0.8}Ge_{0.2}$ (bulk α ~ 180 μV/K) and the Si substrate (ρ ~ 25 Ω cm, with[4] a carrier concentration of ~ $3\times10^{14}/cm^3$, and a bulk α[5] of ~ 600 μV/K). A tentative explanation is offered below for the large α value in the present case. The total thermopower (α) =ΔV/ ΔT = ΔV/(e ΔT) relates to the flow of energy (ΔE = e ΔV) from a hot end to a cold end, and is contributed to by both the electrons and lattice vibrations/phonons. Consequently, α is taken as the sum of an electronic contribution (α_e) and that due to phonons (α_p), *i.e.,* $\alpha = \alpha_p + \alpha_e$. (*i.e.*, in the presence of a current, the scattering of electrons by the phonons tends to preferentially increase the amplitude of the phonons in the direction of electron travel - implying a net contribution from the phonons/lattice vibrations to the α). Due to the larger effective mass of the phonons, α_p is often found to contribute significantly[6] (up to 90% of the total S). For example, for lightly doped Si samples, at 300 K, α values ~ 1000 μV/K has been recorded*, i.e.*, at ~ 10^{16} /cm^3

(Weber *et al*[6]) and at ~ 10^{14} /cm^3 (Geballe *et al*[7]), presumably accounted for by the above "phonon drag" effect. It is also to be noted that the effect of phonons on electron motion is predominant at low carrier concentrations and low temperatures- conditions which offer the maximum electron-phonon interactions.

In the present multilayer samples, we have two parallel conduction channels (the heavily doped $Si_{0.8}Ge_{0.2}$ layer and the relatively insulating Si layer). We hypothesize that the SiGe layer contributes to the low resistivity (ρ) while the Si layer is responsible for the high Seebeck coefficient (α). In this sample, one can expect that the phonon mean free path is restricted by the superlattice period (~ 10 nm) and the drag on the phonons in the Si due to electron transport in the SiGe layer could give rise to a large thermopower (α). α_p is found from theory[8] to be proportional to the fraction of electron momentum transferred from the electrons to the phonons and increases with temperature. This observation might explain the increased " with temperature. The exponential increase in the number of phonons with temperature can be invoked and is plausibly a bigger influence than the interface roughness.

Discussion and Future Work

1. The two probe resistance measurements which includes the whole length of the sample plus the InGa liquid metal sample contacts yields a power factor ("$^2/\rho$) for the $Si_{0.8}Ge_{0.2}$QW films that is in general agreement with previously published Hi-Z data (Ref. _) that simultaneous high Seebeck coefficients of ~800-1300 μV/K and resistivity ~1mS-cm can be obtained on a single sample. With these measured ", and literature thermal conductivity for $Si_{0.8}Ge_{0.2}$ of 0.063 Wcm^{-1}K^{-1} a ZT near room temperature of **~ 5** is realized.
2. The four probe resistance measurement (Figure 1b), yields a resistivity that is ~15 times lower than the two probe Ohmmeter technique, with a corresponding increase in "$^2/\rho$. The difference between could be due to the effect of the probes or contact resistance and is being investigated. Four probe measurements are generally preferred in electrical measurements as the electrical resistance of the leads (in two probe measurements) can interfere and yield larger values of measured resistance and calculated ρ as was observed. Note that in either case, a ZT > 5 is obtained.
3. We have not investigated how many of the ~ 5000 Si/SiGe multi-layers are actually being electrically contacted. It would, of course, be desirable for uniform current distribution and optimal thermoelectric conversion efficiency, to contact all of the layers. This problem is exacerbated by the high difference in resistivity values of the constituent silicon and Si/SiGe layers of the quantum well superlattice. The new high resolution TEM facility at ORNL (Oak Ridge National Laboratory) should be able to help Hi-Z characterize the current flow in QW films using techniques such as EBIC (electron beam induced current) that is used with the SEM (scanning electron microscope) to visually observe current flow in materials and microcircuits. ORNL appears interested in pursuing this work.
4. It is to be noted that the above hypotheses of the contributions of phonon drag to the observed large α can be tested by depositing Si of increasing concentrations in the multilayers ($Si_{1-x}Ge_x$; $0.2< x< 0.8$), in which case, the total measured " would decrease. The relative thicknesses of the SiGe and the Si layers would also change the ρ and " and careful analyses would help in discerning their relative contributions.

4 QUANTUM WELL FILM GROWTH IN LARGE SPUTTERING MACHINE

Kapton film grown on the large sputtering machine was studied by SEM. The SEM of a Si/SiGe grown on Kapton in the large machine is shown on Figure 1 showing that individual Si and SiGe films are not apparent. It is possible that the layers have been inadvertently coated during the ion gun cutting and other samples are being analyzed to determine if the Si and SiGe layers can be identified.

In contrast to quantum well film growth on Kapton, deposition on Si leads to excellent quantum well film distinction and excellent properties. The SEM photographs of Figures 2 and 3 support this.

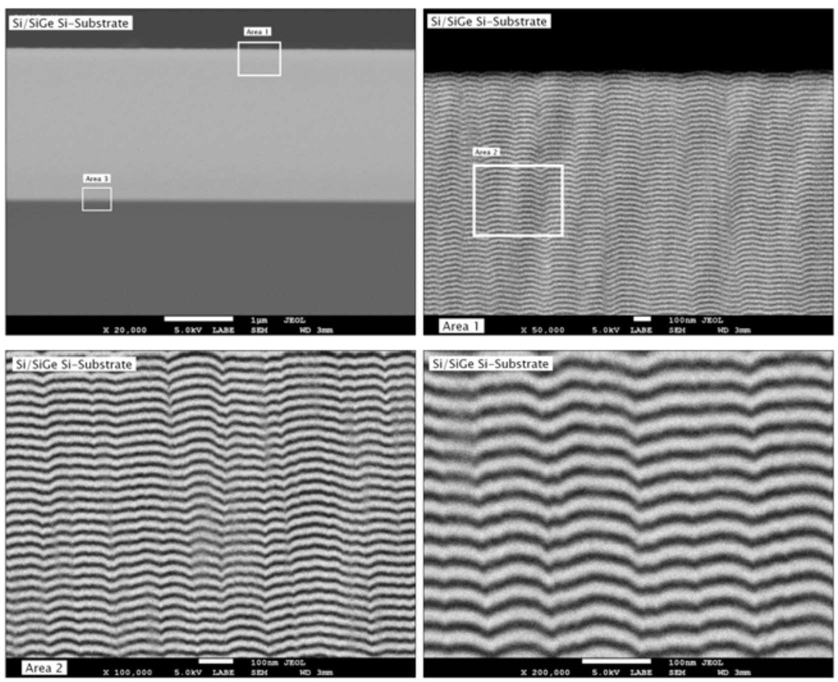

Figure 2. SEM of Si/SiGe films (each at 10 nm or 100Å) grown on a Si substrate in small sputtering machine showing excellent distinction between Si and SiGe layers that leads to excellent thermoelectric properties.

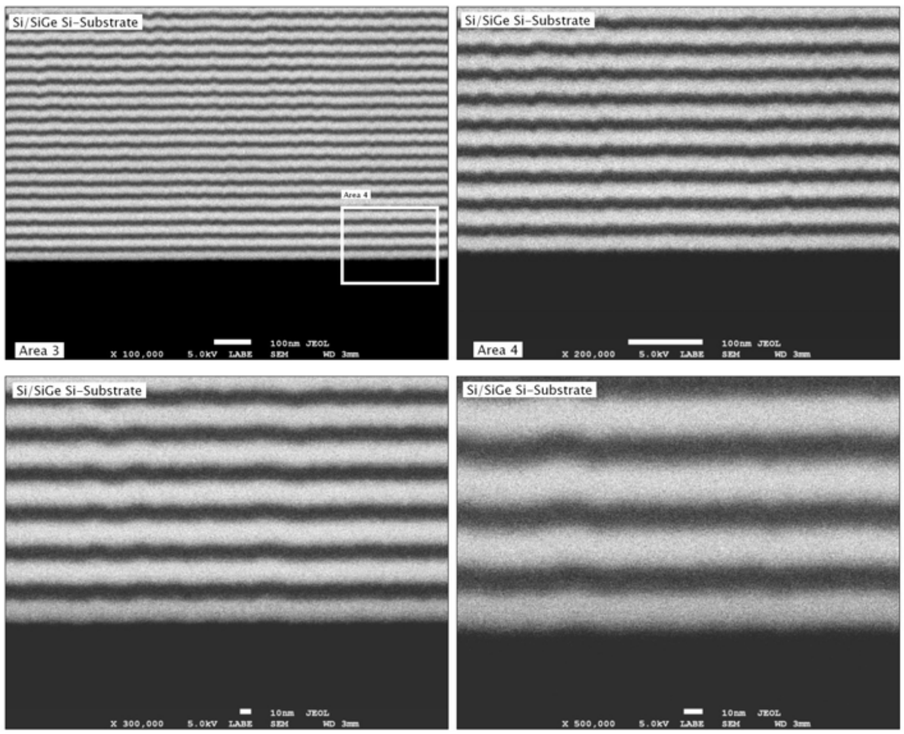

Figure 3. Photo of another excellent film. SEM of Si/SiGe films (each at 10 nm or 100Å) grown on a Si substrate in small sputtering machine showing excellent distinction between Si and SiGe layers that leads to excellent thermoelectric properties.

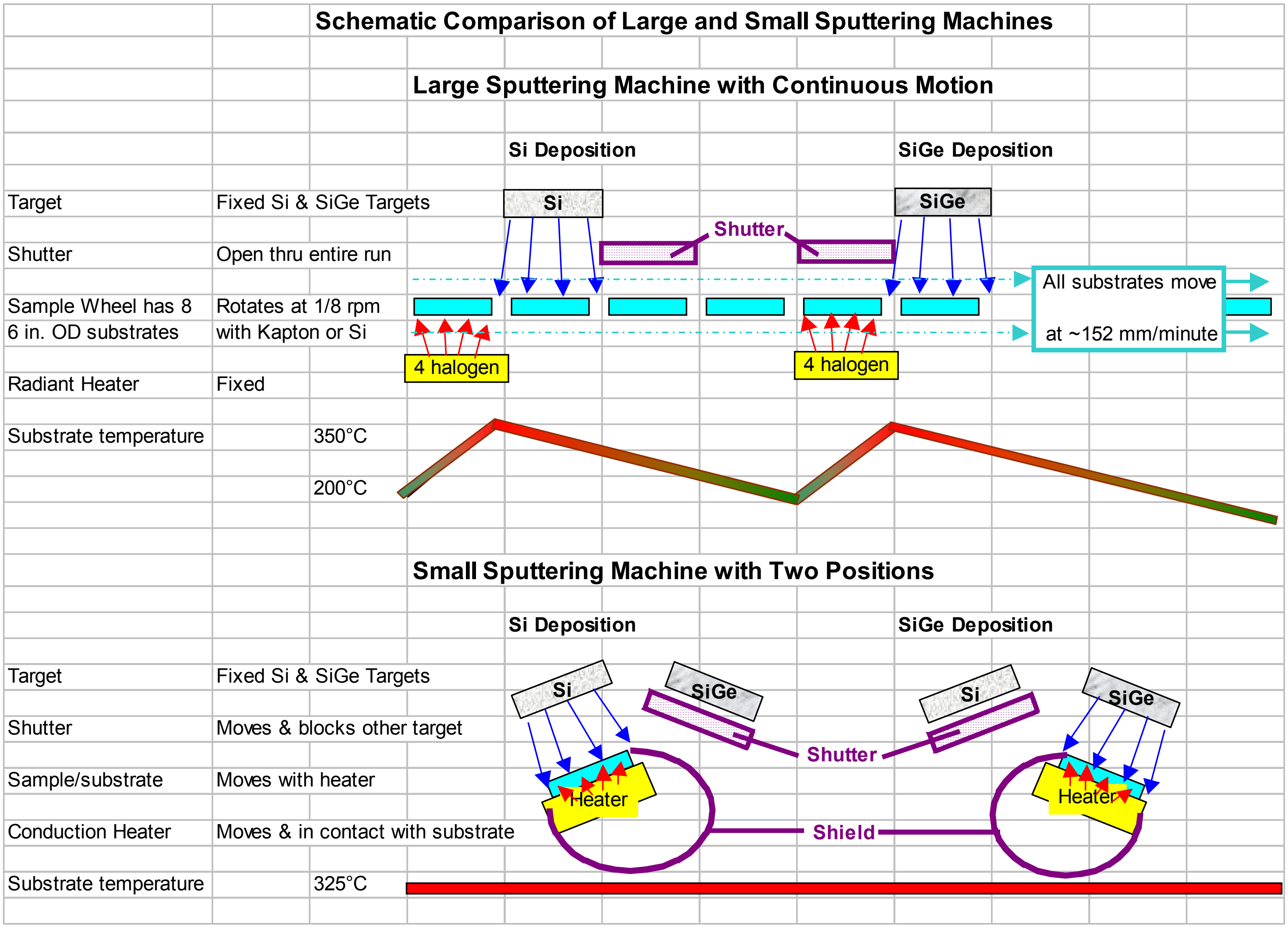

Figure 4. Comparison of Hi-Zs two sputtering machines. Each one is tuned to give 100 Å/minute Si.

At this time, Hi –Z is evaluating whether the differences are due to the differences in the two sputtering machines or the substrate. A schematic of the process to alternately deposit 10 nm or 100 Å Si and SiGe films is shown on Figure 4. Higher resolution SEM will be obtained in late January to resolve as-fabricated film architecture.

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